

**SAMPLING FOR RESIDUES OF MOLINATE
AND THIOBENCARB IN WELL WATER AND
SOIL IN THE CENTRAL VALLEY**

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ABSTRACT

A well survey was conducted in rice-growing areas of California to determine whether molinate (Ordram®) or thiobencarb (Bolero®) residues were detected in ground water. Sampling was conducted in September 1985 by the Environmental Hazards Assessment Program (EHAP), California Department of Food and Agriculture in 127 townships located in 17 counties in the Central Valley. No residues of molinate or thiobencarb were detected in 127 sampled wells. This result was confirmed in a more intensive sampling intended to compare data obtained from different soil types and different ground water basins: no residues were detected in 42 additional wells.

Undisturbed soil cores were taken from two rice fields, one in Colusa County and one in Merced County to determine the soil distribution of molinate and thiobencarb. Sampling occurred in November 1985 approximately six months after pesticide application. Soil at the Colusa County site was a Willows clay with a water table approximately 20 feet from the surface. Molinate was detected down to 26 inches, but the greatest concentration was measured in the first 0-6 inch segment. Concentrations in subsequent segments were lower by approximately an order of magnitude. The soil distribution of thiobencarb was similar to molinate except residues were detected down to 72 inches. Soil concentrations ranged from 28 to 490 ppb and 14 to 950 ppb for molinate and thiobencarb, respectively.

Soil at the Merced County site was a Landlow clay with a perched water table located only five feet below the surface. Molinate was detected only in the first 0-6 inch depth segment at 97 ppb. Thiobencarb was also detected in the surface segment (460 ppb) and once again at the 12-18 inch depth (140 ppb).

The results of the well water survey and the soil sampling study indicated that use of molinate and thiobencarb in rice-growing areas did not pose a hazard to ground water. Residues, measured six months after initial pesticide application, were confined mainly in the first 0-6 inches of soil indicating low soil mobility. The relatively strong attraction of both pesticides to soil, the organic conditions in rice culture and the low permeability of the soils may be factors that mitigate soil movement of molinate and thiobencarb when used to control weeds in rice paddies.

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INTRODUCTION

Molinate and thiobencarb were registered in California in 1972 and 1983, respectively, for control of weeds in rice paddies. Since that time, detection of rice herbicides in Sacramento River water has resulted in studies to determine the effects of rice agricultural practices on the fate of molinate (Ordram®) and thiobencarb (Bolero®) in surface waters (5). Studies have not yet been conducted to determine their potential for movement through soils to ground water. The large amounts of water used in rice production and continuous flooded conditions may increase the likelihood for pesticide movement through soil. Therefore, the Environmental Hazards Assessment Program (EHAP), California Department of Food and Agriculture (CDFA) conducted a well sampling study to determine if residues of molinate or thiobencarb are currently in ground water and a soil coring study to determine the soil distribution of the herbicides after application to commercial rice paddies.

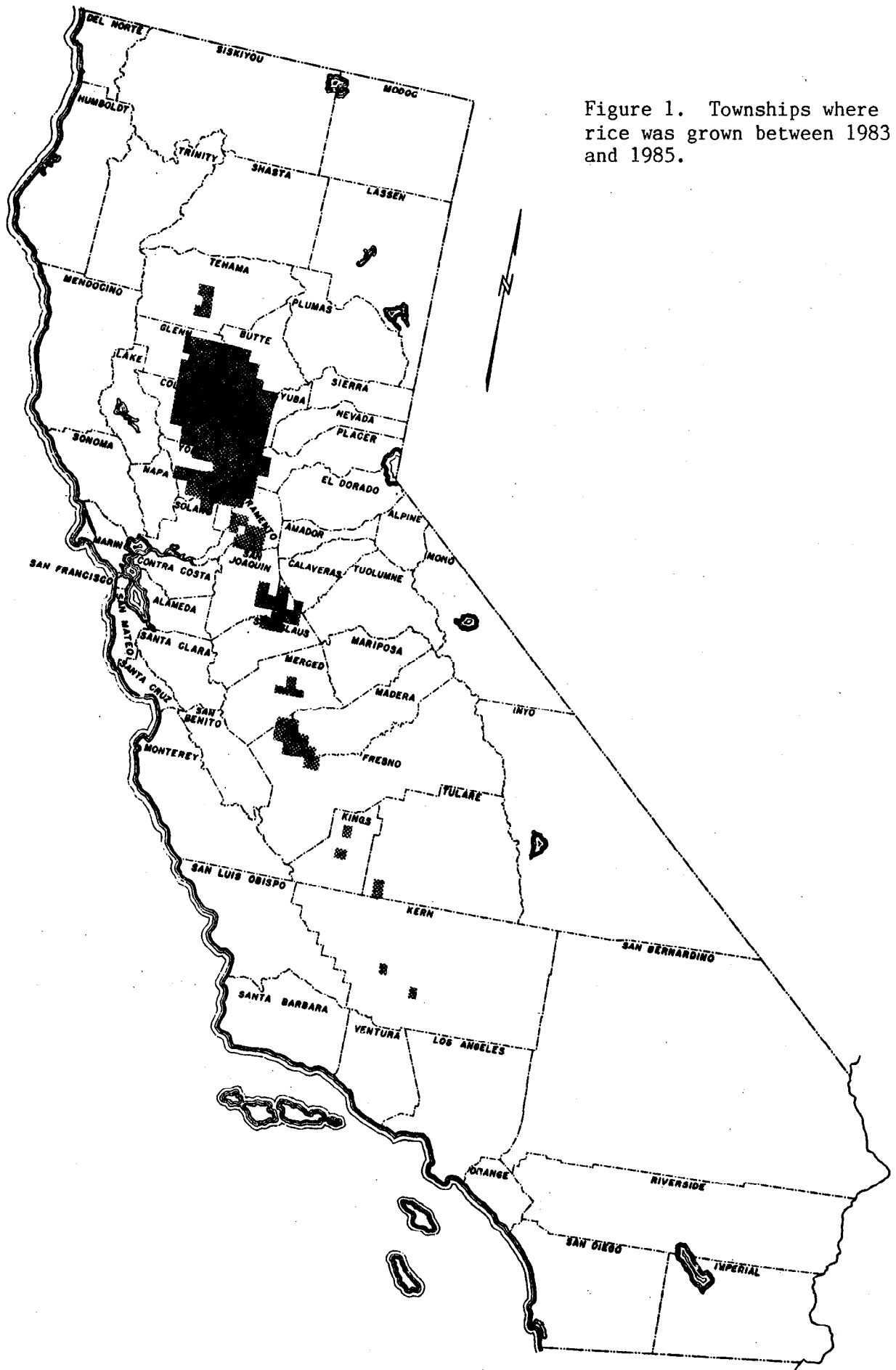
MATERIALS AND METHODS

Study Design

The study was designed first to determine whether molinate or thiobencarb residues were present in ground water and then to determine the soil distribution of the pesticides in commercial rice fields. One hundred-twenty seven townships were identified where rice was grown in the Central Valley and where a suitable well for sampling was located (Figure 1). In order to insure that samples reflected ground water conditions, cased and sealed wells that had well logs were sampled. Additional wells were sampled to provide comparisons between soil types and between locations of ground water basins. The soil type comparison was made by obtaining additional well water samples from three soil classifications in the Sacramento Valley: eight from alluvial soils in Colusa County, seven from flood basin deposits in Colusa County, and eight from the Victor Formation in Sacramento County (2). Since these wells also represented the Sacramento Valley, 19 additional wells were sampled in Merced County for comparison of the Sacramento Valley basin to the San Joaquin Valley basin (1).

Sites for soil sampling were originally to be chosen based on the results of the well survey. Since no well samples were positive for either molinate or thiobencarb, two fields with documented use of molinate and thiobencarb were selected for sampling. One field was located in Colusa County and the other in Merced County. The soil distribution of molinate and thiobencarb was measured in undisturbed soil cores taken to ground water at each field. Analyses for pesticide concentration, soil texture, percent moisture, and organic matter content were conducted on soil samples taken in six-inch increments.

Figure 1. Townships where rice was grown between 1983 and 1985.



Well Sampling

Well logs from the California Department of Water Resources (DWR) were evaluated to identify potential sampling sites. The criteria used for selection of a well were:

1. Quality of well sanitary seal
2. Well use (domestic, irrigation, municipal, other)
3. Well depth and perforation
4. Well location in township

The most important guideline for selecting wells was the quality of the well's sanitary seal. Wells sealed with cement and bentonite materials ranked higher than those with a gravel-packed seal. Also, a minimum depth of 20 feet was preferred to insure that a well was properly sealed. In some townships, only clay-sealed wells that were cable driven were available for sampling. Eighty-seven percent of the wells sampled in the survey had cement or bentonite seals.

Domestic wells were preferred over irrigation and municipal wells because domestic wells generally draw from shallower depths of ground water and are less likely to contain contaminants introduced by lubrication systems found on larger pumping systems (Table 1). Irrigation or municipal wells were sampled when no suitable domestic wells could be located in a township.

The third priority for selecting a well site was the depth of the casing. Wells that drew from the shallowest unconfined ground water aquifer were preferred over deeper cased wells (Table 2). Consideration was made for perforations in the well casing to compensate for very deeply cased wells.

Table 1. Characterization by type of use of all wells sampled.

Area	Number of Wells By Type of Use				
	Number of Wells Sampled	Domestic	Irrigation	Municipal	Other
<u>Well Survey</u>	127	120	3	1	3
<u>Site Contrasts</u>					
Alluvial Soil	10 ^a	7 ^a	0	3	0
Flood basin deposits	8 ^b	5 ^b	0	2	1
Victor Formation	9 ^b	9 ^b	0	0	0
Merced County	20 ^b	20 ^b	0	0	0
 TOTAL	 169	 156	 3	 6	 4

- a. Two wells in this site contrast were also included in the well survey.
b. One well in this site contrast was included in the well survey.

Table 2. Characterization by well depth of all wells sampled.

Area	Number of Wells	Number of Wells in Each Well Depth Range (Feet)										
		15 to 20	21 to 50	51 to 75	76 to 100	101 to 125	126 to 150	151 to 175	176 to 200	201 to 225	226 to 250	251+
<u>Well Survey</u>	127	0	14	18	23	14	11	12	13	3	4	15
<u>Site Contrasts</u>												
Alluvial	10	0	0	1 ^a	2 ^a	0	0	2	1	1	0	3
Flood Basin Deposits	8	0	0	0	0	0	2	0	1	0	2 ^a	3
Victor Formation	9	0	0	0	1	0	3	5	0	0	0	0
Merced County	20	0	0	3 ^a	5	9	1	1	1	0	0	0

a. One well in this site contrast was included in the well survey.

Wells located in the center of a township (Sections 15, 16, 21 and 22) were preferred if all other conditions were met (3). However, a well in an outer section was selected if its well casing was 50 feet or shallower in depth when compared to wells located in the center sections.

Water samples were collected between September 3 and September 19, 1985. Standard EHAP sampling and data collection procedures were followed (7) (Appendix I). Prior to sampling, water was collected from the sampling port in a one-pint wide mouth glass jar to determine pH. Sulfuric acid was added to the samples as a preservative. The volume of sulfuric acid used to adjust the pH in the sample to a value less than 6 was determined from this pre-sample. This procedure was shown in separate degradation studies as an effective method for preventing degradation of molinate and its metabolites (Appendices II and III).

Water samples were collected in one-liter amber glass bottles. The bottle was sealed with aluminum foil in a plastic screw cap, placed in a styrofoam holder, and stored on wet ice. Two samples were collected from each well. However, three samples were collected randomly from 10 percent of the wells for use as quality control samples. These samples were obtained by filling a one gallon stainless steel bucket with well water and then splitting the contents into three one-liter bottles.

Soil Sampling

Undisturbed soil cores were taken with a 20-inch split barrel sampler located in an eight-inch diameter hollow stem auger. The system was motorized and mounted on a Mobile Drill Model B-53 drilling rig. This technique for collecting undisturbed samples has been previously described (10). The split barrel

sampler contained three 6'' x 2.5'' (o.d.) stainless steel cylinders which upon sampling were sealed with aluminum foil and plastic caps, and then stored on dry ice. Prior to analysis, the soil samples were split longitudinally into three sections by an electronically controlled hydraulic pump (10). One portion was used for molinate and thiobencarb residue analysis, one for determination of soil moisture (Appendix IV), and one for determination of organic matter content and soil texture (Appendices V and VI).

Chemical Analysis

Water and soil samples were submitted to California Analytical Laboratory (Cal Lab), West Sacramento, CA to be analyzed for molinate and thiobencarb and their sulfoxide derivatives. Water samples (800 ml) were extracted with two 50 ml portions of dichloromethane. The pooled extracts were concentrated by rotary evaporation to near dryness, transferred to an 8 ml test tube with 1:1 (v:v) hexane:acetone, and exchanged to methanol under a stream of nitrogen to a final volume of 5.0 ml. Soil extraction methods were developed by Cal Lab (Appendix VII). Soil samples (40 g) were extracted with 100 ml of 1:1 (v:v) methanol-dichloromethane. An aliquot of the extract was rinsed with aqueous sodium chloride, concentrated by rotary evaporation with a methanol keeper, and adjusted to a 2.0 ml final volume with methanol. For the extracts that were analyzed with a gas chromatograph (GC) using a nitrogen-phosphorous detector (NPD), the column was 4 ft by 2 mm glass, 10% SP2250, and the temperature was programmed from 160°C to 240°C. For extracts analyzed by High Pressure Liquid Chromatography (HPLC), the column was 25 cm by 4.6 mm Supelco LC-18, solvent was programmed from 25% aqueous acetonitrile to 75% aqueous acetonitrile, and detection was ultra-violet at 220 nm. Reference standards were obtained from Stauffer (molinate, lot M-829-C), IHARA (thiobencarb, lot SQ-063), and CDFA

(both sulfoxides). Minimum detection limits (MDL) for molinate, thiobencarb, molinate sulfoxide and thiobencarb sulfoxide in water samples were 1, 1, 5, and 5 ppb, respectively, for GC analysis and 0.5, 0.5, 0.5, and 10 ppb, respectively, for HPLC analysis. The MDL for soil analysis was 14 ppb for both molinate and thiobencarb. Analyses were not conducted for the sulfoxides in the soil samples.

Quality Control

The analytical interlaboratory quality control program for water samples included 21 samples that were split between Cal Lab and the quality control laboratories and four blind spikes containing equal amounts of thiobencarb and molinate or their sulfoxide derivatives submitted to each laboratory. Spiked samples were included with each extraction set conducted by the main laboratory for use as on-going quality control samples. Methods used by each laboratory are in Appendix VIII.

For soil samples, 10 percent of the positive detections were confirmed by GC-Ion Trap Detector. Also, one spiked sample was included per extraction set for on-going quality control. In addition, a standard soil analysis was performed on each extraction set and 20 percent of the positives were subject to 5-replicate HPLC runs.

RESULTS

Well Samples

No residues of molinate or thiobencarb were detected and confirmed in any of the well water samples. Samples from three domestic wells originally were indicated as positive for molinate by HPLC at 0.59 ppb, 0.93 ppb, 3.0 ppb. However, these well samples were not confirmed by GC at a minimum detection limit of 1.0 ppb nor were residues detected in the replicate samples by either HPLC or GC. These wells were also resampled and analyzed by Cal Labs and Stauffer Chemical Company, Richmond, CA and again residues were not detected in duplicate analyses. The original detections were considered false positives. Well water samples taken for the soil and ground water basin comparison were also negative, so the comparisons could not be statistically analyzed. But the data did reaffirm the results of the larger well survey indicating no detectable residues of molinate or thiobencarb in ground water.

Soil Analysis

Undisturbed soil cores were obtained from one rice field in Colusa County and from one rice field in Merced County. The field in Colusa County had been cropped in rice the previous five years with molinate and/or thiobencarb applied each year. Both molinate and thiobencarb had been applied in the spring of 1985, as a post flood granular application at 2.5 and 4 pounds per acre (lb/acre), respectively. The field in Merced County had a similar history of rice production, except that it had been fallow in 1983. Only thiobencarb had been applied in the spring of 1985 at 4 lbs/acre. Molinate had been applied in 1984 at a rate of 5 lbs/acre.

The soil at the Colusa County site was a Willows clay, characterized as fairly well-drained and originating from shale and sandstone material. Soil near the surface is neutral in pH but becomes alkaline (pH 8.5) at around the 60-inch depth (4). Soil texture analyses of the cores indicated that although there was some fluctuation, clay content generally ranged between 40 and 60% and sand content ranged between 10 and 20% down to the 132-138 inch depth (Table 3). At this depth, clay content decreased and ranged between 25 and 50% and sand content increased and ranged between 30 and 40%. Organic matter content was around 4% in the surface segment and then consistently decreased with depth ranging below 1% at the 52-58 inch depth (Figures 2 and 3).

Residues of molinate and thiobencarb were detected (MDL at 14 ppb) in both cores taken from the Colusa County site. The cores were taken down to approximately 20 feet but the residues were detected near the surface of the core (Table 4). The greatest concentrations were measured in the first 0-6 inch segment with molinate at 465 ppb and thiobencarb at 865 ppb. Molinate was detected in subsequent segments down to the 20-26 inch depth and thiobencarb was detected down to the 66-72 inch depth. The concentrations of both pesticides in the subsurface segments were approximately one order of magnitude lower than that measured at the 0-6 inch depth. Both molinate and thiobencarb were measured at the 86-92 inch depth in core two but the sudden appearance of both pesticides at that depth indicated possible contamination of that sample.

The soil at the Merced County site was a Landlow clay, characterized as a soil that drains poorly and imperfectly and derived from basic igneous rock along with alluvium of mixed origin (8). Complete drainage is inhibited by a clay layer beneath the surface and a cemented layer of lime underneath. The same

Table 3. Texture analysis of the percentage of sand, silt, and clay particles and percent organic carbon found by segment in two soils core drilled to a depth of 252 inches in Colusa County.

Segment Depth (inches)	Core 1				Core 2			
	Texture Analysis			% Organic Matter	Texture Analysis			% Organic Matter
	Sand	Silt	Clay		Sand	Silt	Clay	
0 - 6	10.2	34.0	55.8	4.3	--	--	--	---
6 - 12	10.2	33.0	56.8	2.9	9.2	33.0	57.8	3.4
12 - 18	12.2	28.0	59.8	3.1	9.2	32.0	58.8	2.1
20 - 26	30.2	28.0	41.8	1.1	10.2	32.0	57.8	2.5
26 - 32	27.2	25.0	47.8	0.9	11.2	29.0	59.8	2.3
32 - 38	-- (a)	--	--	---	20.2	26.0	53.8	---
40 - 46	--	--	--	---	--	--	--	---
46 - 52	18.2	31.0	50.8	1.0	12.2	29.0	58.8	1.5
52 - 58	15.2	30.0	54.8	0.8	21.2	26.0	52.8	1.1
60 - 66	15.2	29.0	55.8	0.9	15.2	30.0	54.8	0.8
66 - 72	12.2	33.0	54.8	0.8	17.2	31.0	51.8	0.6
72 - 78	15.2	28.0	56.8	0.8	--	--	--	---
80 - 86	12.2	38.0	49.8	0.3	16.2	34.0	49.8	0.5
86 - 92	12.2	35.0	52.8	0.5	18.2	38.0	43.8	0.3
92 - 98	14.2	38.0	47.8	0.2	22.2	36.0	41.8	0.8
100 - 106	--	--	--	---	16.2	27.0	56.8	0.3
106 - 112	--	--	--	---	10.2	26.0	63.8	0.3
112 - 118	--	--	--	---	14.2	29.0	56.8	0.2
120 - 126	12.2	33.0	54.8	0.2	16.2	32.0	51.8	0.2
126 - 132	10.2	34.0	55.8	0.2	8.2	35.0	56.8	0.1
132 - 138	10.2	35.0	54.8	0.2	10.2	39.0	50.8	0.2
140 - 146	26.2	34.0	39.8	0.1	29.2	31.0	39.8	0.1
146 - 152	34.2	32.0	33.8	---	31.2	33.0	35.8	0.1
152 - 158	40.2	31.0	28.8	0.2	30.2	39.0	30.8	0.1
160 - 166	--	--	--	---	--	--	--	---
166 - 172	--	--	--	---	51.2	24.0	24.8	0.1
172 - 178	--	--	--	---	--	--	--	---
180 - 186	40.2	27.0	32.8	0.1	35.2	27.0	37.8	0.1
186 - 192	42.2	27.0	30.8	0.1	30.2	31.0	38.8	0.1
192 - 198	40.2	29.0	30.8	0.1	37.2	28.0	34.8	0.1
200 - 206	24.2	36.0	39.8	0.1	35.2	26.0	38.8	0.1
206 - 212	36.2	25.0	38.8	0.1	38.2	28.0	33.8	0.1
212 - 218	--	--	--	---	41.2	27.0	31.8	0.1
220 - 226	--	--	--	---	40.2	30.0	29.8	0.1
226 - 232	19.2	31.0	49.8	0.1	32.2	35.0	32.8	0.1
232 - 238	--	--	--	---	46.2	26.0	27.8	0.1
240 - 246	27.2	29.0	43.8	0.1	--	--	--	---
246 - 252	28.2	32.0	39.8	0.2	--	--	--	---

(a). No analysis.

Figure 2. Histogram comparing soil texture and organic matter content by soil segment to a depth of 252 inches.

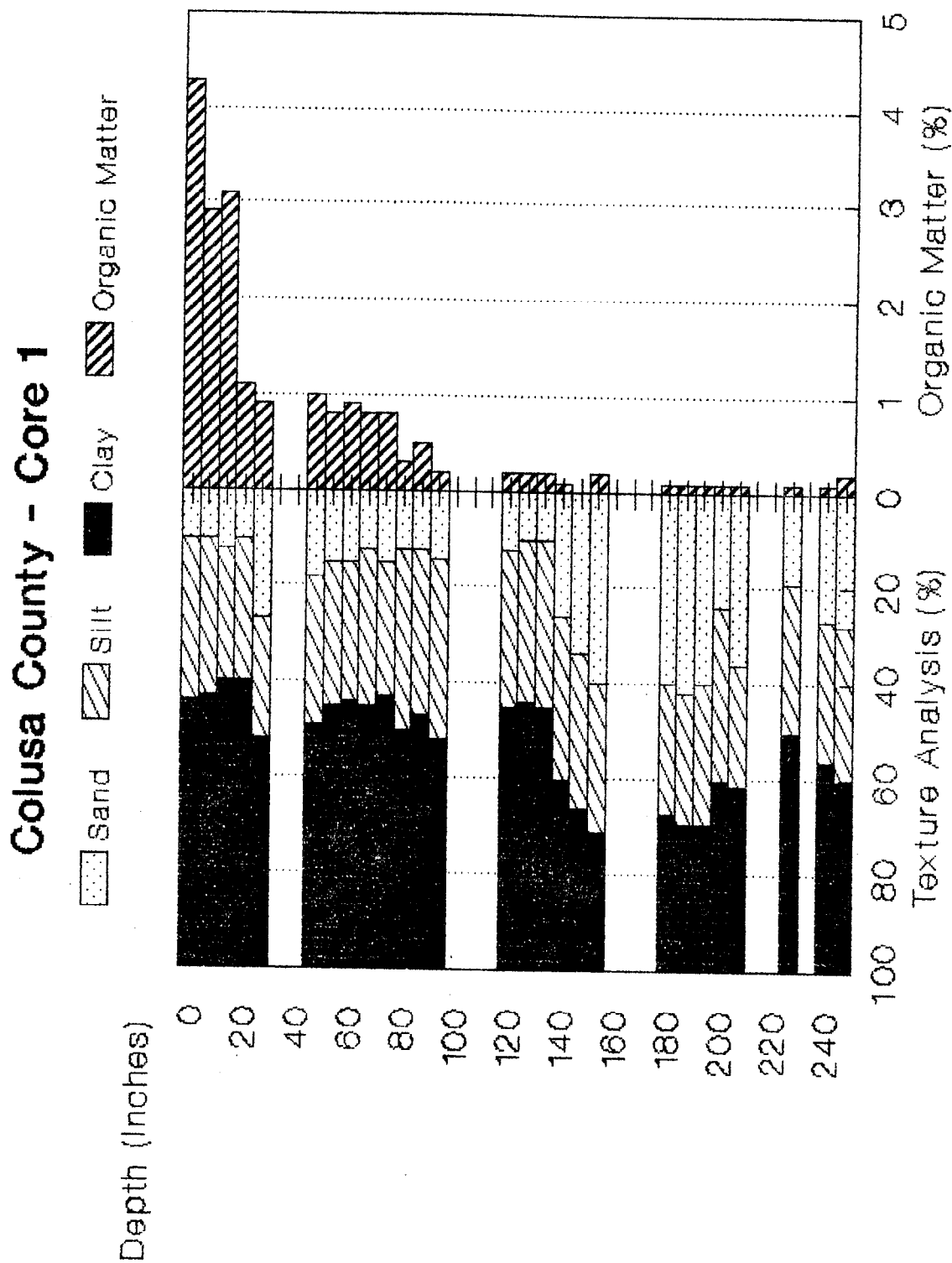


Figure 3. Histogram comparing soil texture and organic matter content by soil segment to a depth of 240 inches.

Colusa County - Core 2

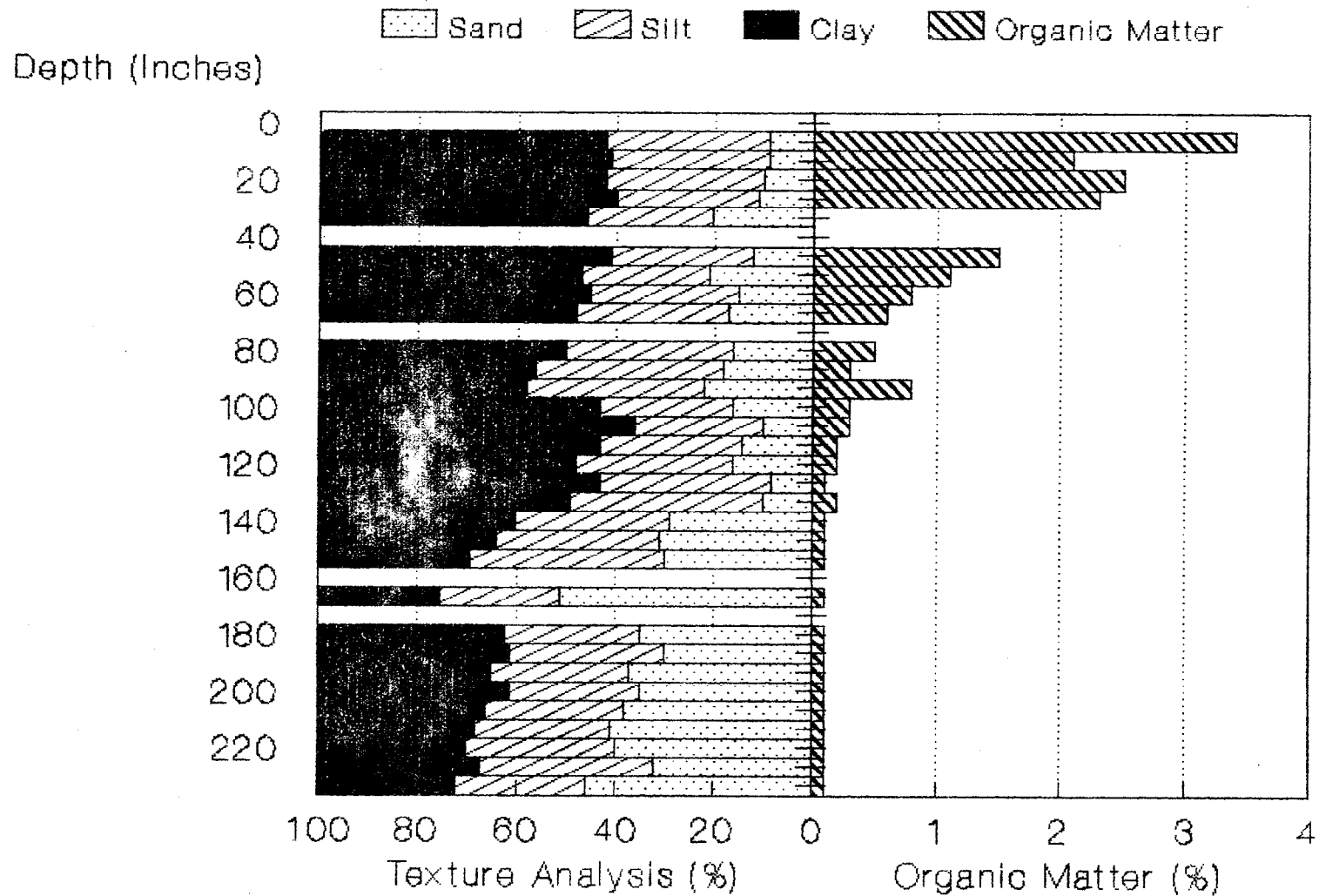


Table 4. Concentration in ppb of thiobencarb and molinate in 2 soil cores taken in Colusa County.

Segment Depth (inches)	Core 1		Core 2	
	Thiobencarb	Molinate	Thiobencarb	Molinate
0 - 6	820	490	910	440
6 - 12	26	61	16	19
12 - 18	27	54 ^a	38	23
20 - 26	17	ND ^a	32	28
26 - 32	15	ND	17	ND
32 - 38	ND	ND	ND	ND
40 - 46	16	ND	19	ND
46 - 52	ND	ND	16	ND
52 - 58	14	ND	ND	ND
60 - 66	ND	ND	ND	ND
66 - 72	14	ND	ND	ND
72 - 78	ND	ND	ND	ND
80 - 86	ND	ND	ND	ND
86 - 92	ND	ND	17	15
92 - 98	ND	ND	ND	ND
100 - 106	ND ^b	ND	ND	ND
106 - 112	--	--	ND	ND
112 - 118	--	--	ND	ND
120 - 126	ND	ND	ND	ND
126 - 132	ND	ND	ND	ND
132 - 138	ND	ND	ND	ND
140 - 146	ND	ND	ND	ND
146 - 152	ND	ND	ND	ND
152 - 158	ND	ND	ND	ND
160 - 166	--	--	ND	ND
166 - 172	--	--	ND	ND
172 - 178	--	--	--	--
180 - 186	ND	ND	ND	ND
186 - 192	ND	ND	ND	ND
192 - 198	ND	ND	ND	ND
200 - 206	ND	ND	ND	ND
206 - 212	ND	ND	ND	ND
212 - 218	--	--	ND	ND
220 - 226	ND	ND	ND	ND
226 - 232	ND	ND	ND	ND
232 - 238	--	--	ND	ND
240 - 246	ND	ND	--	--
246 - 252	ND	ND	--	--

(a). None detected. Minimum detection limit was 14 ppb.

(b). No analysis.

general trend in soil texture was observed in the core taken from the Merced County site that was observed in the cores at the Colusa County site. Clay content was generally between 40 and 50% down to the 40-46 inch depth after which it decreased with measurements mainly between 10 and 20% (Table 5). The sand content was again the converse of clay content ranging between 10 and 20% down to the 40-46 inch depth and generally increasing to between 40 and 65% below that depth. The organic matter content was 2.2% in the 0-6 inch depth and below 1% in subsequent samples (Figure 4).

Pesticide residues were detected only in two segments. Both molinate and thiobencarb were measured at the 0-6 inch depth at 460 and 97 ppb, respectively (Table 6). Only thiobencarb was measured at the 12-18 inch depth at 14 ppb. This pattern reflected the differences in yearly application of the pesticide at the site; thiobencarb was applied in 1985 and molinate was applied in 1984.

Quality Control Analyses

For water samples, the recovery rate for on-going spiked samples included in all extraction sets were good for the parent compounds but were low for the sulfoxide metabolites (Appendix VIII, Table VIII-1). With respect to interlaboratory samples, results from all laboratories for the 21 split samples were none detected. All laboratories also correctly identified the four blind spiked samples with good recovery rates (Appendix VIII, Table VIII-2). Recovery of molinate and thiobencarb from the soil sample spikes were very good (Appendix VIII, Table VIII-3).

Table 5. Texture analysis of the percentage of sand, silt, and clay particles found by segment in a soil core drilled to a depth of 200 inches at Field 2 - Core 1 in Merced County.

Segment Depth (inches)	Texture Analysis			% Organic Matter
	Sand%	Silt%	Clay%	
0 - 6	16.2	36.0	47.8	2.2
6 - 12	16.2	33.0	50.8	0.8
12 - 18	61.2	25.0	13.8	0.5
20 - 26	13.2	39.0	47.8	0.3
26 - 32	17.2	38.0	44.8	0.4
32 - 38	15.2	37.0	47.8	0.3
40 - 46	16.2	42.0	41.8	0.3
46 - 52	60.2 ^a	28.0	11.8	0.4
52 - 58	---	---	---	---
60 - 66 ^b	71.2	24.0	4.8	0.2
66 - 72	---	---	---	---
72 - 78	---	---	---	---
80 - 86	47.2	41.0	11.8	0.0
86 - 92	57.2	34.0	8.8	---
92 - 98	52.2	34.0	13.8	0.1
100 - 106	---	---	---	---
106 - 112	---	---	---	---
112 - 118	---	---	---	---
120 - 126	22.2	55.0	22.8	0.1
126 - 132	23.2	53.0	23.8	---
132 - 138	26.2	36.0	37.8	0.1
140 - 146	52.2	31.0	16.8	0.1
146 - 152	55.2	30.0	14.8	---
152 - 158	17.2	39.0	43.8	0.1
160 - 166	64.2	23.0	12.8	0.0
166 - 172	58.2	27.0	14.8	0.1
172 - 178	64.2	24.0	11.8	0.1
180 - 186	66.2	24.0	9.8	0.0
186 - 192	48.2	32.0	19.8	0.1
192 - 198	54.2	27.0	18.8	0.1

(a). No analysis.

(b). Perched water table encountered at 60 inches.

Figure 4. Histogram comparing soil texture and organic matter content by soil segment to a depth of 200 inches.

Merced County - Single Core

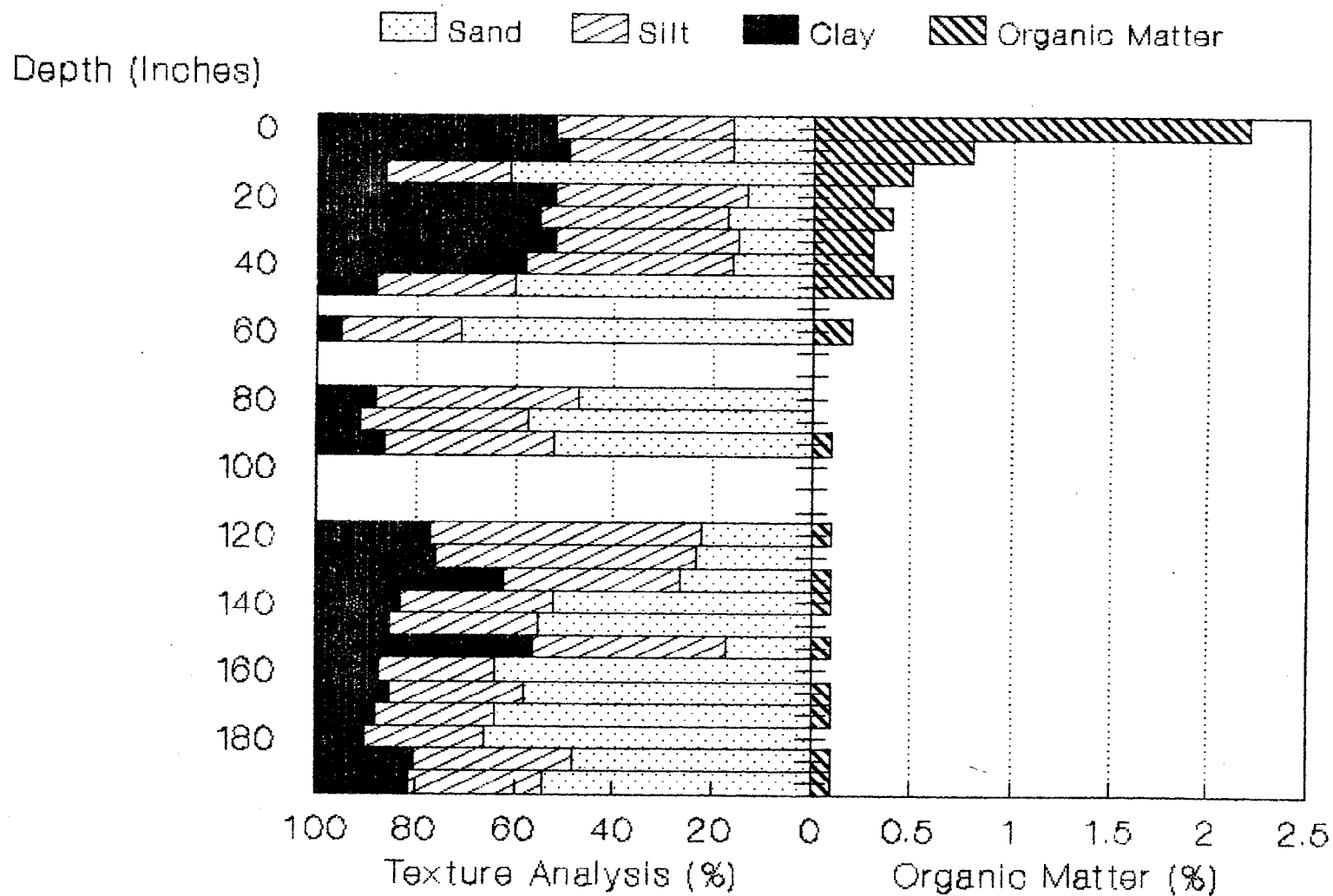


Table 6. Distribution of thiobencarb and molinate in a soil core drilled in Merced County.

Segment Depth (inches)	Residue Analysis	
	Thiobencarb	Molinate
0 - 6	460	97
6 - 12	ND ^a	ND
12 - 18	14	ND
20 - 26	ND	ND
26 - 32	ND	ND
32 - 38	ND	ND
40 - 46	ND	ND
46 - 52	ND	ND
52 - 58	ND ^b	ND
60 - 66	ND ^b	ND
66 - 72	ND ^c	ND
72 - 78	---	---
80 - 86	ND	ND
86 - 92	ND	ND
92 - 98	ND	ND
100 - 106	---	---
106 - 112	---	---
112 - 118	---	---
120 - 126	ND	ND
126 - 132	ND	ND
132 - 138	ND	ND
140 - 146	ND	ND
146 - 152	ND	ND
152 - 158	ND	ND
160 - 166	ND	ND
166 - 172	ND	ND
172 - 178	ND	ND
180 - 186	ND	ND
186 - 192	ND	ND
192 - 198	ND	ND

(a). None detected. Minimum detection limit was 14 ppb.

(b). Perched water table encountered at 60 inches.

(c). No analysis.

DISCUSSION

Molinate and thiobencarb or their sulfoxide breakdown products were not detected in well water samples taken from rice and growing areas of the Central Valley. Wells were sampled that were cased and sealed and in good condition to insure that samples reflected ground water conditions. A total of 169 wells were sampled in 127 townships located in 17 counties. Samples were acidified with sulfuric acid to prevent breakdown of the pesticides during storage. A degradation study conducted to test the effectiveness of this procedure indicated no significant breakdown of the parent compounds when stored over a 55 day period in the acid buffer solution. Tests for the metabolites were conducted over an 18-hour period and again no breakdown was measured in the acid buffer solution.

Soil coring occurred approximately 6 months after pesticide application to the rice paddies. Residues were detected but they were restricted to the surface soil indicating low mobility. The amounts of organic matter (OM) found in the soils in the two rice fields were higher than soils in areas of known contamination. Studies by Zalkin et al. (10) and Welling et al. (9) detected movement of compounds through soil containing around 1% OM in the surface segments and around 0.1% OM in the subsurface soil profile. Both molinate and thiobencarb have greater Koc values than bromacil (152-948, 2738-19870, and 69-77 ml/g for molinate, thiobencarb, and bromacil, respectively) (6,9). This combination of organic matter content and soil adsorption of molinate and thiobencarb could cause residues to remain attracted to surface segments, thereby retarding downward movement.

On the other hand, one might have expected to find molinate deeper in the soil profile than thiobencarb because it has a lower K_{oc} and higher water solubility than thiobencarb (water solubility of 800 and 30 ppm for molinate and thiobencarb, respectively) (5). Results from this study indicated that thiobencarb was deeper in the soil profile. This could partially be explained by differences in yearly applications and different application rates at the sites. Ross et al. (5) in a mass balance study also measured higher concentrations of thiobencarb in the soil after a shorter duration. In rice-paddies, greater water solubility and lower soil attraction may cause a greater portion of applied pesticides to be lost in the tailwater. Also, greater volatility of molinate could cause an upward gradient during periods of flooding. Thus, there may be greater amounts of thiobencarb available for downward movement after periods of flooding.

Overall, this combination of relatively high amounts of percent OM in a clay soil and the pesticides' strong attraction to soil could have prevented the movement of molinate and thiobencarb through the soil profile. The absence of molinate and thiobencarb residues in well water also indicated low soil mobility of these pesticides when used to control weeds in rice paddies. If levels of organic matter in soils in other rice-growing areas are similar to this study, then the likelihood of downward movement of thiobencarb and molinate in soil in other rice-paddies would be low.

Literature Cited

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- (6) Sachs, E.S. 1976. Comparative soil sorption, movement, and volatility of three thiocarbamate herbicides. M.S. thesis. University of California, Davis.
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- (10) Zalkin, F., M. Wilkerson and R.J. Oshima., 1984. Pesticide Movement to Groundwater. Volume II. Pesticide Contamination in the Soil Profile at DBCP, EDB, Simazine, and Carbofuran Application Sites. California Department of Food and Agriculture. Sacramento, CA. 168 pp.

Appendix I

Chains of Custody for Well and Soil Core Studies

STATE OF CALIFORNIA
DEPARTMENT OF FOOD
AND AGRICULTURE

CHAIN OF CUSTODY RECORD
(use ball point pen only)

ENVIRON. MONITOR. & PEST MGMT.
ENVIRON. HAZARDS ASSESSMENT
1220 N STREET, ROOM A-149
SACRAMENTO, CA 95814

Study #	Sample #	Well Number			Tract No.	County #	Date Sampled				Person Collecting	Study area	Well Location	Sample Point			
		Twn	Rng	Sec			Mo	Day	Yr	Time				Tank	Pump	Other	
	4 0																

Minutes Pumped	Replicate #	Units	Units	Units	Units	Chemist	Lab #

Partner:

Location:

Lab Results:

Save extracts

Owner:

Remarks:

Thiobencarb (Bolero)

Sulfoxide

Molinate (Ordram)

Sulfoxide

Chemist:

Date:

KEY

Col. 1

S = Spike

Col. 2

* = Split

Col. 33

A =

B =

C =

(etc.)

Col. 34-36 (location)

01 =

02 =

03 =

(etc.)

Col. 37-39

T = Tank

P = Pump

0 = Other

Relinquished for Lab by: (Signature)	Date/Time
Received by: (Signature)	Relinquished by: (Signature)
Received by: (Signature)	Relinquished by: (Signature)
Received by: (Signature)	Relinquished by: (Signature)
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Received for Lab by: (Signature)	Date/Time
	Lab #

Distribution: Original & One Copy Accompanies Shipment, copy to Coordinator Field Files.

ENVIRON. MONITOR. & PEST MGMT.
ENVIRON. HAZARDS ASSESSMENT
1220 N STREET, ROOM A-149
SACRAMENTO, CA 95814

Partner:	Location:	Lab Results:	Save extracts												
Remarks:		Thiobencarb (Bolero)													
		Sulfoxide													
		Molinate (Ordram)													
		Sulfoxide													
		Chemist:	Date:												
<div style="text-align: center;"><u>KEY</u></div> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><u>Col. 1:</u> S = Spike</p> <p><u>Col. 2:</u> * = Split</p> <p><u>Col. 5:</u> 1 = field #1 2 = field #2 3 = field #3</p> </div> <div style="width: 45%;"> <p><u>Col. 6:</u> 1 = core #1 2 = core #2 3 = core #3</p> <p><u>Col. 79-80:</u> FA = Food & Ag CA = Cal Labs AP = APPL</p> </div> </div>		<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%;">Relinquished for Lab by: (Signature)</td> <td style="width: 50%;">Date/Time</td> </tr> <tr> <td>Received by: (Signature)</td> <td>Relinquished by: (Signature)</td> </tr> <tr> <td>Received by: (Signature)</td> <td>Relinquished by: (Signature)</td> </tr> <tr> <td>Received by: (Signature)</td> <td>Relinquished by: (Signature)</td> </tr> <tr> <td>Received by: (Signature)</td> <td>Relinquished by: (Signature)</td> </tr> <tr> <td>Received for Lab by: (Signature)</td> <td>Date/Time</td> </tr> </table>		Relinquished for Lab by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Received by: (Signature)	Relinquished by: (Signature)	Received by: (Signature)	Relinquished by: (Signature)	Received by: (Signature)	Relinquished by: (Signature)	Received for Lab by: (Signature)	Date/Time
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Appendix II

Molinate and Thiobencarb Degradation in Water Samples

Appendix II

Molinate and Thiobencarb Degradation in Water Samples

This study was set up to test the stability of molinate and thiobencarb in water samples at acidic and basic pH values.

Study Design

Spikes were made up in buffer solutions at two levels of acidity:

Acid - 0.5 ppm each Thiobencarb and Molinate at pH = 5.5

Base - 0.5 ppm each Thiobencarb and Molinate at pH = 9.2

The spiked buffer solutions were placed into one liter amber bottles which were stored in the dark at ambient temperature. Ten-ml aliquots were removed and analyzed at 1 week intervals for 2 months. Standards were made up in hexane and stored at -10° centigrade. All analyses were done in triplicate.

Analytical Method

Ten mls of water was placed into a screwtop test tube. Five mls of hexane was added and the test tube agitated for 10 minutes. A portion of the hexane layer was removed and analyzed by gas chromatography.

Instrument Conditions

Varian 3700 GLC equipped with a thermionic specific detector 10 meter 5% Phenyl-Methyl Megabore Column (0.54 mm i.d.) Injector = 230C; Detector = 230C; Column flow = 25 mls/min; Oven initial = 100C held for 3 minutes then 30 c/min to 220C.

Results of Degradation Study

The results of the molinate and thiobencarb degradation study in water samples are in Table II-1. Mean values, standard deviations, and standard errors of the means were calculated for each observation period during the molinate and thiobencarb degradation study (Tables II-2 and II-3). An analysis of variance was performed on the mean values over time to determine if a significant loss of molinate or thiobencarb occurred during the 55 day storage period. No significant loss of molinate or thiobencarb was revealed by a Type I Mean Square Test in either an acidic or base solution during the test period (Table II-4).

Table II-1. Molinate and Thiobencarb parent compound degradation in acid and basic solutions. Results of analyses performed in study from August 27 to October 21, 1985 (55 days).

No. Days	% REMAINING OF INITIAL 0.5 PPM PARENT COMPOUND			
	ACID (pH = 5.5)		BASE (pH = 9.2)	
	Molinate	Thiobencarb	Molinate	Thiobencarb
0	86,80	85,82	88,78,82	72,68,74
7	74,78	79,82	74,76	76,79
13	69,77,76	79,82,83	72,70,65	74,75,67
20	68,65,70	70,70,74	72,73,72	74,72,73
30	72,80,82	87,84,85	82,86,82	84,82,84
41	76,76,74	73,78,71	74,68,71,74	78,70,76
49	73,70,75	80,72,70	77,71,68	80,73,75
55	69,74,70	75,73,68	74,70,73	75,71,72

Table II-2. Mean values, standard deviations, and standard errors of the means for percent of Molinate and Thiobencarb parent compound remaining during degradation in an acid buffer solution (pH 5.5).

Time (Days)	Molinate				Thiobencarb			
	N	Mean	Standard Deviation	Standard Error of The Mean	N	Mean	Standard Deviation	Standard Error of The Mean
0	2	83.0	4.24	3.00	2	83.5	2.12	1.49
7	2	76.0	2.83	2.00	2	80.5	2.12	1.49
13	3	74.0	4.35	2.51	3	81.3	2.08	1.20
20	3	67.6	2.52	1.45	3	71.3	2.31	1.33
30	3	78.0	5.29	3.05	3	85.3	1.53	0.88
41	3	75.3	1.15	0.66	3	74.0	3.61	2.08
49	3	72.6	2.51	1.44	3	74.0	5.29	3.05
55	3	71.0	2.65	1.52	3	72.0	3.61	2.08

Table II-3. Mean values, standard deviations, and standard errors of the means for percent of Molinate and Thiobencarb parent compound remaining during degradation in an base buffer solution (pH 9.2).

Time (Days)	Molinate				Thiobencarb			
	N	Mean	Standard Deviation	Standard Error of The Mean	N	Mean	Standard Deviation	Standard Error of The Mean
0	3	82.6	5.03	2.90	3	71.3	3.05	1.76
7	2	75.0	1.41	1.00	2	77.5	2.12	1.50
13	3	69.0	3.60	2.07	3	72.0	4.36	2.51
20	3	72.3	0.58	0.33	3	73.0	1.00	0.57
30	3	83.3	2.31	1.33	3	83.3	1.15	0.66
41	4	71.8	2.87	1.43	3	74.7	4.16	2.40
49	3	72.0	4.58	2.64	3	76.0	3.61	2.08
55	3	72.3	2.08	1.20	3	72.7	2.08	1.02

Table II-4. Results of the ANOVA Type I Mean Square test for the parent compounds of molinate and thiobencarb during a 55 day degradation study in an acid and base buffer solution.

Type I Mean Square								
Source of Variation	Acid				Base			
	DF	Molinate	DF	Thiobencarb	DF	Molinate	DF	Thiobencarb
Time								
Linear	1	36.45	1	83.71	1	24.48	1	2.25
Quadratic	-	---	-	---	-	---	-	---
Residual	6	19.06	6	21.55	6	28.61	6	17.75

Appendix III

Molinate and Thiobencarb Sulfoxide Dissipation in Drinking Water

Appendix III

Molinate and Thiobencarb Sulfoxide Dissipation in Drinking Water

This study was set up to test the stability of Thiobencarb and Molinate sulfoxides in water samples at acidic and basic pH values.

Study Design

Spikes were made up in buffer solutions at two levels of acidity:

Acid - 1 ppm each molinate and thiobencarb at pH= 4.7

Base - 1 ppm each molinate and thiobencarb at pH= 9.4

Spikes were placed into 1 liter amber bottles which were stored in the dark at ambient temperature. A 10 ml aliquot was removed from each bottle and analyzed at 100 minute intervals for 18 hours. Standards were made up in hexane and stored at -10° Centigrade. Only one sample of each buffer was analyzed at each time interval.

Analytical Methods and Instrument Conditions

The analytical method and instrument conditions are identical to those used for the molinate and thiobencarb degradation study described in Appendix III.

Results of Degradation Study

Results for the sulfoxide degradation study indicated significant degradation in basic but not acidic solutions (Table III-1). No replication was performed on this study which was 1080 minutes in duration. The degradation in basic solution was curvilinear (Table III-2).

Table III-1. Sulfoxide compound degradation in acid and base solutions.

Time (minutes)	% Remaining of Initial 1 ppm			
	Acid (pH 4.7)		Base (pH 9.4)	
	Molinate Sulfoxide	Thiobencarb Sulfoxide	Molinate Sulfoxide	Thiobencarb Sulfoxide
0	92	92	92	80
100	81	93	77	61
200	80	87	56	34
300	70	70	44	17
400	74	80	30	<0.07 mdl
500	67	63	20	<0.07 mdl
600	76	80	15	<0.07 mdl
700	74	77	11	<0.07 mdl
800	80	--	9	<0.07 mdl
1080	84	77	14	<0.07 mdl

NOTE: Levels of sulfoxide less than 0.07 were undetectable and for statistical purposes were considered as a zero value. No replication was performed in this analysis.

Table III-2. Results of the ANOVA Type I Mean Square test for the sulfoxide compounds of molinate and thiobencarb during a 1080 minute degradation study in an acid and base buffer solution.

Type I Mean Square							
Source of Variation	Acid				Base		
	DF	Molinate	DF	Thiobencarb	DF	Molinate	DF Thiobencarb
Time							
Linear	1	14.09	1	210.29	1	6157.93**	1 5081.17**
Quadratic	-	---	-	---	1	1667.95**	1 2401.58**
Residual	8	56.94	7	79.80	7	2.81	7 56.69

** Significant at $p = 0.01$.

Appendix IV

Procedure for Soil Moisture Determination

Procedure for Soil Moisture Determination

Equipment used:

Quadruple beam balance
soil drying cans with lids
spatula
oven with thermometer
asbestos gloves

Procedure:

- * Make all weight measurements to .01 gram
- * Record tare weight of weighing cans
- * Add approximately 25 grams of soil sample to can and record weight (this is wet wt. of soil plus can wt.)
- * Place uncovered in 105 to 110°C oven for 24 hours
- * Remove and cap. Let sit half hour or more until cooled to room temperature
- * Record weight (this is dry wt. of soil plus can wt.)

Formula for % moisture:

$$\% \text{ moisture} = \frac{(\text{wet wt.} - \text{tare wt.}) - (\text{dry wt.} - \text{tare wt.})}{\text{dry wt.} - \text{tare wt.}} \times 100$$

Appendix V

Procedure for Determination of Percent Organic Matter in Soil

ORGANIC MATTER (O.M.)¹

Dichromate reduction

EQUIPMENT

Soil grinder of non-ferrous material (mullite mortar and pestle)

0.5 mm screen (40-60 mesh)

Erlenmeyer Flasks, 500 ml

Thermometer, 200°C

Bunson burner or electric hot plate

Reagents

1. Potassium dichromate solution, 1.0 N. Dissolve 49.04 g of dry reagent grade potassium dichromate, ($K_2Cr_2O_7$) in distilled water and dilute to 1 liter.
2. Sulfuric acid-silver sulfate solution. Dissolve 25 g of reagent grade silver sulfate (Ag_2SO_4) in 1 liter of reagent grade concentrated 36 N sulfuric acid.
3. Ortho-phenanthroline ferrous sulfate indicator solution. Dissolve 1.485 g of 1,10-phenanthroline monohydrate (Eastman Kodak No. 3239) and 0.695 g of ferrous sulfate ($FeSO_4$) in distilled water and dilute to 100 ml.
4. Ferrous sulfate solution 0.5 N. Dissolve 140 g of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) in distilled water, add 15 ml of reagent grade concentrated H_2SO_4 . Cool and dilute to 1 liter.

Procedure

1. Grind soil to pass 0.5 mm screen.
2. Weigh 5.00 g of soil into 500 ml flask. We used from 1 to 5 grams of soil.
3. Add 10 ml Reagent 1 and then 20 ml Reagent 2; both reagents are conveniently dispensed from burettes.
4. Mix well by swirling; insert thermometer and heat gently over burner or on hot plate to reach a temperature of 150°C in one minute. Swirl contents continuously while heating to avoid local super-heating and consequent decomposition of dichromate. (The heating time and temperature must be adhered to.)
5. Remove from heat and cool.
6. Add approximately 200 ml of water.
7. Add 3-4 drops of Reagent 3.
8. Titrate with Reagent 4 to sharp red endpoint. Record ml titration as "A".
9. Standardize Reagent 4 for each set of samples by running 10 ml of Reagent 1 through the procedure. Record titration as "B".
10. Calculate percent organic matter.

Calculations

$$\text{Percent Organic Matter} = (B-A) \times \frac{10}{B} \times 0.58/\text{g of soil used}$$

Remarks

If more than 80% of the dichromate is reduced, "A" < 4 ml, the determination should be repeated using less soil.

The factor, 0.58 is derived from:

the milliequivalent weight of carbon, 0.003;

the assumption that this method gives 89% recovery of organic carbon in soils;

the assumption that the organic matter of soils contains 58% carbon.

If difficulty is experienced in obtaining a distinct endpoint, it will be helpful to filter the digest at Step 5: After cooling, add 100 ml of water, filter through Whatman No. 2 on a Buchner funnel, washing with another 100 ml of water. Then proceed with Step 7.

1. Rauschkolb, Dr. Roy. Soil Analysis Method - Organic Matter: Dichromate Reduction. California Fertilizer Association Handbook of Soil Analysis Method, Section 18.0.

Appendix VI

Procedure for Soil Texture Determination

Hydrometer Method Improved for Making Particle Size Analyses of Soils¹

PROCEDURE

The procedure in detail is as follows: Dissolve 50 g. Calgon in a liter of distilled water. Pour 100 cc. of this solution into a pint jar. Add 50 g. of air-dry soil (100 g. in the case of very sandy soil). Mix thoroughly and let stand in covered jar overnight or 15 to 20 hours. Then wash contents into the soil cup (Figure 1) with distilled water. Fill the cup with water to within 3 inches from the top. Connect cup to the dispersing machine and stir for 2 minutes. Disconnect cup and wash contents into soil cylinder using a water jet from the plastic bottle. Fill soil cylinder to the liter mark. Bring cylinder and contents to 68°F. by placing in a water bath. Remove cylinder and close mouth with rubber stopper. With right hand holding and pressing on the stopper, and left hand holding the bottom of the cylinder, turn cylinder completely upside down and back 20 times. Return cylinder to water bath and immediately start a timer or stop watch. Quickly put 3 drops of amyl alcohol on top of soil suspension column to dissipate froth and at 15 seconds gently place hydrometer in the soil suspension column and prepare to take a hydrometer reading at 40 seconds. Remove the hydrometer and wash it. The last hydrometer reading is to be taken after sedimentation has continued for exactly 2 hours.

Temperature affects the hydrometer readings and since the hydrometer has been calibrated at 68°F. the soil cylinder with contents should be kept in a bath at this temperature or an attempt should be made to work close to this temperature. In fact, the ideal place to conduct mechanical analyses of soils by the hydrometer method is in a 68°F. constant temperature room. Where temperature correction has to be made, multiply differences in temperature above or below 68°F. by a factor or 0.2. The product above 68° is added to the hydrometer reading and the product below 68° is subtracted. Use of the correction factor is permissible only within the temperature range 60 to 76°F.

When floating in a 0.5% solution of Calgon (100 cc. 5% solution diluted to 1 liter) the hydrometer has a stem reading of 6.5. This reading must be subtracted from every hydrometer reading obtained with soil suspensions prepared in the described manner.

To calculate the amounts of combined sands, of silt, and of clay as determined by the hydrometer method the procedure is as follows for the U.S. Department of Agriculture soil particle size classification:

The corrected hydrometer reading at the end 40 seconds is divided by the amount of dry soil taken and multiplied by 100. This result is the percentage of material still in suspension at the end of 40 seconds. This percentage is subtracted from 100 and the result is this percentage of material that settled out at the end of 40 seconds, which represents all the sand in the soil (2.00 - 0.05 mm). The corrected hydrometer reading at the end of 2 hours is also divided by the dry weight of the soil and multiplied by 100. The result is percentage of material still in suspension at the end of 2 hours and is the clay (below 0.002 mm). The percentage of silt (0.05-0.002 mm) is obtained by difference.

At the conclusion of the 2-hour hydrometer reading, the suspension is washed on a No. 300 sieve. That portion retained by the sieve is dried and analyzed on a set of sieves consisting of one each of No. 20, 40, 60, 140, and 200.

1. Bouyoucos, George J. 1962. Hydrometer Method Improved for Making Particle Size Analysis of Soils. Agronomy Journal, vol. 54.

Appendix VII

Method Development For HPLC Soil Analysis

Appendix VII

Development of HPLC Method - Soil Samples

Three samples were submitted to Cal Lab to determine the accuracy of the proposed HPLC method under consideration. Samples from the top and another portion of the core were analyzed to estimate their range of concentrations. Levels were determined and then duplicate soil samples were spiked with 100 ppb of molinate and thiobencarb. The results (ppb with percent recovery) for these analyses are as follows:

Table VII-1. Results of HPLC method development.

Sample I.D.	<u>ppb Found (Percent Recovery)</u>	
	<u>Molinate</u>	<u>Thiobencarb</u>
Method blank	<10	<10
Location 1, Core 1	<10	14
100 ppb spike (a)	81 (81%)	93 (79%)
100 ppb spike dup (a)	88 (88%)	92 (78%)
Location 1, Core 1 - Top	380	870
Location 2, Core 1	<10	<10

(a) This is a matrix spike. Soil from sample Location 1, Core 1 was spiked with 100 ppb molinate and 100 ppb thiobencarb. The percent recovered (value in parentheses) is determined by subtracting the amount found in the matrix (soil sample) from the amount found in the spike analysis and dividing by 100.

These results were sent to CDFA for consideration and by terms of the contract with Cal Lab, CDFA returned an outline to Cal Lab containing a methods validation protocol. CDFA recommended three spike levels (at 20 ppb, 100 ppb, 500 ppb) to be analyzed in ten fold replication (30 samples) for method validation. The amount of thiobencarb recovered was higher than molinate at the three levels of fortification for the method validation spikes (Table VII-4).

Table VII-2. Results of method validation spikes.

Spike Level	Molinate concentration (ppb)			Thiobencarb concentration (ppb)		
	Recovery(%)	X10	S.D.	Recovery(%)	X10	S.D.
20 ppb	82.5	16.5	3.27	117.0	23.3	2.06
100 ppb	86.1	86.1	9.50	99.4	99.4	6.38
500 ppb	82.4	412.0	49.84	93.4	467.0	21.11

These recovery rates were considered good for soil sample analysis and the method was accepted for use by CDFA.

Appendix VIII
Quality Control Analyses

Appendix VIII
WELL WATER ANALYSES

Interlaboratory Methods

Chevron studies used a GC-NPD with a 6 foot OV 101 column. Chevron analyzed for thiobencarb but no thiobencarb sulfoxide analyses were performed due to a miscommunication by CDFA requesting Chevron to do so.

Stauffer performed their analyses on a Hewlett-Packard Model 5880A capillary gas chromatograph equipped with a nitrogen-phosphorus detector. The column was a HP bonded Dimethyl Silicone with dimensions 12 m x 0.20 mm and 0.33 micron film thickness.

Cal Lab method was as described in Materials and Methods.

Quality Control Analyses

Recovery rates for on-going spiked samples included in all extraction sets were good for the parent compound but were low for the sulfoxide metabolites (Table VIII-1).

Twenty-one split samples analyzed by Chevron were determined to contain no measurable levels of thiobencarb. Chevron's internal quality control procedures produced an average recovery rate of 97.65 percent for four fortifications of 5 ppb thiobencarb made in distilled water. Four blind spike samples were delivered to Chevron. Chevron identified three of the four spikes submitted to them by CDFA and their recovery rate averaged 102%. The fourth spike was not detected because they did not analyze for thiobencarb sulfoxide (Table VIII-2).

Table VIII-1. California well survey for rice herbicides (molinate and thiobencarb). Analysis of spiked samples submitted to California Analytical Laboratory.

Spike/Method	Number of Observations(N)	Percent Recovery	
		Mean	Standard deviation
Molinate 3 ppb parent spike HPLC	17	82	24
Molinate 3 ppb parent spike GC	17	73	21
Thiobencarb 3 ppb parent spike HPLC	17	99	11
Thiobencarb 3 ppb parent spike GC	17	86	18
Molinate 30 ppb parent spike HPLC	10	85	10
Molinate 30 ppb parent spike GC	10	67	11
Thiobencarb 30 ppb parent spike HPLC	10	103	4
Thiobencarb 30 ppb parent spike GC	10	78	8
Molinate 15 ppb sulfoxide spike HPLC	17	47	15
Molinate 15 ppb sulfoxide spike GC	17	64	15
Thiobencarb 15 ppb sulfoxide spike HPLC	-- (a)	--	--
Thiobencarb 15 ppb sulfoxide spike GC	17	64	10
Molinate 50 ppb sulfoxide spike HPLC	10	57	10
Molinate 50 ppb sulfoxide spike GC	10	88	8
Thiobencarb 50 ppb sulfoxide spike HPLC	10	62	31
Thiobencarb 50 ppb sulfoxide spike GC	10	79	19
Combined			
Molinate 3,30 ppb parent HPLC	27	83	20
Molinate 3,30 ppb parent GC	27	71	18
Thiobencarb 3,30 ppb parent HPLC	27	101	9
Thiobencarb 3,30 ppb parent GC	27	83	15
Molinate 15,50 ppb sulfoxide HPLC	27	51	14
Molinate 15,50 ppb sulfoxide GC	27	73	17
Thiobencarb 15,50 ppb sulfoxide HPLC	-- (b)	--	--
Thiobencarb 15,50 ppb sulfoxide GC	27	70	16

(a) No results due to difficulty encountered with procedure.

(b) Not available. No recovery data for thiobencarb sulfoxide 15 ppb HPLC.

Table VIII-2. Comparison of analyses of blind spiked water samples for molinate and thiobencarb by three different laboratories. Percent recoveries shown in parentheses.

Concentration (ppb) and compound in spiked samples	Pesticide concentrations (ppb) in water samples analyzed by:			
	Chevron Lab G C	Stauffer Lab G C	California Analytical Lab G C HPLC	
3.0 ppb thiobencarb	3.1 (103)	3.9 (130)	2.8 (93)	3.5 (117)
3.0 ppb molinate	- (-)	4.0 (133)	2.8 (93)	3.2 (107)
20.0 ppb thiobencarb	19.7 (99)	20.4 (102)	21.0 (105)	21.0 (105)
20.0 ppb molinate	- (-)	20.7 (104)	14.0 (70)	16.0 (80)
50.0 ppb thiobencarb	52.1 (104)	53.6 (107)	40.0 (80)	36.0 (72)
50.0 ppb molinate	- (-)	52.6 (105)	78.0 (156)	53.0 (106)
50.0 ppb thiobencarb sulfoxide	- (-)	- (-)	35.0 (70)	41.0 (82)
50.0 ppb molinate sulfoxide	- (-)	78.0 (156)	29.0 (58)	33.0 (66)

Note: A dash (-) in a column indicates that no analysis was performed for that specific spike.

Stauffer analyzed 25 samples for thiobencarb and molinate and 13 of the 25 samples for molinate sulfoxide. Four of the twenty-five samples were blind spiked samples containing thiobencarb, molinate, and molinate sulfoxide. No thiobencarb, molinate or molinate sulfoxide was found in any of 21 quality control split samples. Stauffer identified all four CDFA blind spikes with an average recovery rate of 119.8% (Table VIII-2).

Stauffer performed their own quality assurance tests to determine the average recovery rates for thiobencarb, molinate, and molinate sulfoxide. Molinate recoveries averaged 103% and thiobencarb 104%. Fortifications of molinate sulfoxide in distilled water and a sample preserved with sulfuric acid averaged 97%, however, samples not preserved with the acid yielded recoveries of 50%.

The Cal Lab quality control results showed that six of the 21 split samples contained an unknown chemical that was originally identified as thiobencarb sulfoxide. However, this was determined to be a false positive by GC-MS. No molinate or thiobencarb was detected in any of the split water samples. Cal Lab was supplied with four blind spikes and identified all four with an average recovery rate of 90.6% by GC and 91.9% by HPLC (Table VIII-2).

Also, Cal Lab reported that the HPLC technique gave an identification of thiobencarb sulfoxide in 38 samples. These results were consistently not confirmed by GC-NPD, and determined to be a false positive. Further analysis indicated that the detection may have been caused by contamination but the source could not be identified.

SOIL ANALYSIS

Quality Control

Overall, 93 ± 6 percent of the molinate and 110 ± 25 percent of the thiobencarb was recovered from the seven 100 ppb blind spikes run with the extraction sets (Table VIII-3). Standard soil analysis indicated a coefficient of variation of 32% for molinate and 28% for thiobencarb (Table VIII-4). The three five-replicate HPLC runs observed molinate and thiobencarb coefficients of variation ranging from 3 to 11 percent and 5 to 10 percent respectively (Table VIII-5).

Table VIII-3. Quality control results of soil spike level 100 ppb.

Spike	Molinate		Thiobencarb	
	ug/kg (ppb found)	Percent recovered	ug/kg (ppb found)	Percent recovered
1	100	100	140	140
2	100	100	140	140
3	97	97	130	130
4	85	85	87	87
5	87	87	88	88
6	94	94	88	88
7	92	92	100	100
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Number of observations	7		7	
Mean X7	93.6		110.4	
Standard deviation	6.0		25.2	

Table VIII-4. Quality control results of standard soils. A standard soil refers to a large, homogeneous sample which can be analyzed several times. Mean and standard deviations are given at the bottom of the table.

Aliquot	ug/kg (ppb found)	
	Molinate	Thiobencarb
1	19	44
2	60	55
3	59	37
4	49	78
5	33	63
6	50	70
7	47	85
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Number of observations	7	7
Mean X7	45.3	61.7
Standard deviation	14.6	17.5

Table VIII-5. Quality control results of five fold replicate HPLC runs.

Sample I.D.		% Moisture	ug/kg (ppb) found	
			Molinate	Thiobencarb
Five fold replicate HPLC*	1A	29	500	820
	1B	29	480	760
	1C	29	490	730
	1D	29	490	730
	1E	29	540	820
X5		29.0	500.0	772.0
S.D.		0.0	23.5	45.5
Five fold replicate HPLC	17A	31	440	910
	17B	31	430	810
	17C	31	420	910
	17D	31	450	880
	17E	31	430	900
X5		31.0	434.0	882.0
S.D.		0.0	11.4	42.1
Five fold replicate HPLC	1A	24	61	26
	1B	--	62	28
	1C	--	51	24
	1D	--	50	22
	1E	--	51	28
X5		--	55.0	25.6
S.D.		--	6.0	2.6

* This sample was also confirmed by mass spectroscopy.